

Phase Equilibrium Relations in the Binary System Bismuth Sesquioxide-Niobium Pentoxide

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The phase equilibrium diagram for the binary system bismuth sesquioxide-niobium pentoxide has been constructed from observations of fusion characteristics and X-ray diffraction data. In the system five binary compounds were observed with $\text{Bi}_2\text{O}_3\text{:Nb}_2\text{O}_5$ ratios of 5:3, 1:1, 4:9, 1:5, and 1:6. The 1:1 compound was found to transform irreversibly (in laboratory time) from the orthorhombic bismutotantalite type structure to a triclinic form at about 1,020 °C and melt congruently at 1,245 °C. The 5:3 compound melts incongruently at 1,193 °C the 4:9 at 1,183 °C and the 1:6 at 1,242 °C. The 1:5 compound has a maximum temperature of stability at 1,095 °C and the 4:9 and 1:6 compounds have minimum temperatures of stability at 1,070 °C and 1,002 °C respectively. Nb_2O_5 was found to enter into solid solution in Bi_2O_3 , up to about 23.5 mole percent Nb_2O_5 . The melting point is increased and the monoclinic-cubic phase transformation temperature is decreased. A morphotropic phase change occurs at about 19.5 mole percent Nb_2O_5 from the cubic to a pseudocubic structure.

1. Introduction

A study of phase relationships in the binary system $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ has been conducted as part of a program of fundamental phase equilibria studies of ceramic materials. Attempts to synthesize an orthorhombic BiNbO_4 compound isostructural with the mineral bismutotantalite have been reported as failures by several workers [1, 2].¹ Aurivillius [2] has indicated that the resultant material was triclinic. No systematic attempt to study the phase equilibrium relations in the entire binary system has been previously published.

X-ray diffraction data, together with the melting points of the compounds and the solidus and liquidus temperatures at various compositions across the system have been obtained in order to construct an equilibrium diagram.

2. Sample Preparation and Test Methods

The following starting materials were employed for the preparation of specimens:

Nb_2O_5 —high-purity grade niobium pentoxide. Spectrographic analysis indicated less than about 0.01 percent Si, 0.001 percent Ca and Mg, with As, Cu, and Ta only questionably present.

Bi_2O_3 —Reagent grade bismuth sesquioxide. Spectrographic analysis indicated less than about 0.01 percent Fe and Si, 0.001 percent Al and Pb, and 0.0001 percent Ag, Ca, Cr, Cu, Mg, and Mn, with Co questionably present.

For the preparation of the specimens the weight percentages were calculated to within ± 0.01 percent, with no corrections made for percentage purity of

the raw materials except for loss on ignition. The starting materials were weighed to the nearest ± 0.1 mg, in sufficient quantities to yield 3 g batches. For most compositions each batch was mixed in a mechanical shaker for about 15 min and pressed into a disk in a $\frac{3}{8}$ in. diam mold at 10,000 lb/in.² The disks were sandwiched between Pt foil disks, stacked in a MgO crucible and calcined in air to 700 °C for either 3 or 6 hr in an electrically heated furnace. Some compositions were prepared by grinding a slurry of the weighed mixture and alcohol with an agate mortar and pestle for a few minutes. The slurry was then allowed to dry in air or dried under an infrared lamp, or in a drying oven, then pressed into a pellet and fired in the usual manner.

Following the preliminary heat treatment the disks were ground in an agate mortar, remixed, and a portion of the specimen reformed in a $\frac{5}{8}$ in. mold at 10,000 lb/in.² and reheated to a desired temperature.

Subsolidus as well as melting point data were obtained by the quenching technique on samples sealed in platinum tubes. An electrically heated vertical tube furnace wound with 80 percent Pt–20 percent Rh wire was used for the quenching experiments. The furnace was controlled by an a-c Wheatstone bridge controller which was capable of holding the temperature to at least ± 2 °C for an extended period of time. Temperatures were measured with a Pt versus Pt 10 percent Rh thermocouple which had been calibrated against the melting points of NaCl (800.4 °C [3]) and Au (1,063 °C [4]). The thermocouple was recalibrated several times during the course of the work. When the tubes were opened the specimens were examined for physical appearances of melting. Specimens were

¹Figures in brackets indicate the literature references at the end of this paper.

suspended in the furnace by fine Pt wire. In order to quench, the wire was burned off, allowing the sealed tubes to drop out of the heating chamber into a beaker of water. The first sign of glazing of the surface of the specimen was interpreted as the first experimental evidence for the solidus temperature. Acceptance of this appearance as evidence of melting was found justified in many specimens by an abrupt difference in the X-ray diffraction patterns of the specimens. The formation of a concave meniscus, without the formation of relatively large crystals, indicated the liquidus temperature. The precision of the temperature measurements for the experimental data points is about $\pm 2^\circ\text{C}$ and the overall accuracy of the reported temperatures is probably about $\pm 5^\circ\text{C}$.

Equilibrium was considered to have been obtained when the X-ray diffraction patterns of specimens successively heated for longer times and/or at higher temperatures showed no change. X-ray diffraction powder patterns were made using a high angle recording Geiger counter diffractometer and nickel-filtered copper radiation, with the Geiger counter traversing the specimen at $\frac{1}{4}^\circ 2\theta/\text{min}$ and the radiation being recorded on the chart at $1^\circ 2\theta/\text{in.}$ The unit cell dimensions reported can be considered accurate to about ± 2 in the last decimal place listed.

3. Compounds in the $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5$ System

3.1. Bi_2O_3

Four polymorphs of Bi_2O_3 have been reported. The equilibrium and stability relations have been somewhat confused mainly because Bi_2O_3 reacts with almost any container, and also because the high-temperature forms are difficult or impossible to quench.

a. Low-Temperature Monoclinic Modification

It has been recognized by several workers [5, 6, 7, 8] that the monoclinic form is the true low-temperature stable modification. The structure of this phase has been described by Sillen [6,9] who has shown by single crystal studies that, although the powder pattern can be indexed on the basis of orthorhombic symmetry, the true symmetry is monoclinic. The indexed X-ray diffraction powder pattern has been given by Sillen [6] and by Swanson et al. [10].

b. High-Temperature Cubic Modification

The monoclinic form of Bi_2O_3 transforms reversibly to a high-temperature form above 700°C . This transformation was first reported by Guertler [5] to be at 704°C using DTA apparatus, but since the composition of the container was not stated the results of this work were questioned by Schumb and Rittner [7]. Apparently only Pt can be used as a container for Bi_2O_3 at any appreciable temperature without fear of considerable contamination. Schumb and Rittner [7], using Pt containers found a temperature of 710°C as the transformation point. However, they postulated that the high-temperature form was tetragonal.

DTA and high-temperature X-ray data (to be reported in more detail in a future publication) have shown that the Bi_2O_3 used in this study transforms from monoclinic to cubic at $730 \pm 5^\circ\text{C}$, this phase remaining stable to the melting point at $825 \pm 5^\circ\text{C}$. However, on cooling the cubic form of Bi_2O_3 , it was observed that the monoclinic phase did not reform at 730°C . Instead, the cubic phase supercooled to about 650°C , then transformed to a tetragonal phase before reverting again to the monoclinic form at about 450°C .

The cubic form has an X-ray diffraction powder pattern resembling that of a face-centered cubic cell of about 5.5 Å. However Sillen [6] has pointed out that it is probably simple cubic with ordered oxygen vacancy positions somewhat similar to the cubic forms of Sb_2O_3 and As_2O_3 .

c. Metastable Tetragonal Modification

A tetragonal form, structurally related to the cubic modification, was first reported by Sillen [6] who prepared it by very fast cooling of Bi_2O_3 vapor. It was also prepared by Schumb and Rittner [7] by a different method of condensation of a vapor. Both workers used a graphite furnace. The tetragonal form could not be obtained in this laboratory by condensing Bi_2O_3 vapors from a Pt dish of molten Bi_2O_3 onto a glass slide. It is still not known whether the graphite is necessary for obtaining the tetragonal form at room temperature. DTA and high-temperature X-ray patterns made in this laboratory on pure Bi_2O_3 indicate that under the conditions of the experiments the tetragonal form only occurs on cooling of the cubic form. It is found only in the range of 650 to 450°C where the monoclinic form is the stable phase.

Sillen [6] reported the unit cell dimension of the tetragonal phase to be $a=10.93$ Å, $c=5.62$ Å, and Schumb and Rittner [7] obtained $a=10.93$ Å, $c=5.63$ Å. In the present study the tetragonal form was obtained at room temperature by quenching, from 773°C , a mixture of 99 mole percent Bi_2O_3 and 1 mole percent Nb_2O_5 . The unit cell dimensions of this phase are $a=10.938$ Å, $c=5.632$ Å.

d. Metastable Body-Centered Cubic Phase(s)

Sillen [6] first reported the occurrence of a body-centered cubic phase ($a=10.08$ Å), which he found by fusing Bi_2O_3 in a porcelain crucible. He recognized that this phase was probably impure, and considered it to be a compound of Bi_2O_3 and a second metal oxide in the proportion of about 12 Bi^{+3} ions to one other metal cation. Schumb and Rittner [7] were able to prepare a body-centered cubic phase ($a=10.245$ Å) which they considered to be a metastable form of pure Bi_2O_3 ($z=13$) different from Sillen's phase. However, this phase could only be made by moderately fast cooling of the previously formed tetragonal phase. It should be pointed out here that even this "pure bismuth oxide" body-centered cubic phase may well have had some carbon atoms present in the lattice, since the

original tetragonal material had been prepared in a graphite crucible. In this laboratory a body-centered cubic phase has been found to occur in a large number of binary systems containing Bi_2O_3 . The thermal stability of the phases found in these systems will be discussed in a future publication.

3.2. Compound $5\text{Bi}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$

A compound was found in the present study at a ratio of $5\text{Bi}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$. The X-ray diffraction powder pattern listed in table 1 can be partially indexed on the basis of a tetragonally distorted pyrochlore type structure with a c/a ratio less than one. The pseudotetragonal parameters are $a=10.912$ Å, $c=10.496$ Å. If the c axis is doubled (20.992 Å) then the relatively strong peak at 6.99 Å can be indexed as (003). However, this larger value does not account for all the extra peaks and the true symmetry is probably less than tetragonal. It should be noted that the powder pattern is always of quite poor quality regardless of the temperature from which the specimen is quenched or the length of time at which the specimen is held at temperature. This phenomenon is often indicative of a nonquenchable phase transformation and may indicate that the compound is actually tetragonal somewhat above room temperature.

The X-ray diffraction powder pattern of the compound $5\text{Bi}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$ is similar to that of the pseudotetragonally distorted pyrochlore previously found for $3\text{PbO} \cdot \text{Nb}_2\text{O}_5$ [11]. However, in the latter compound the c/a ratio is greater than one instead of less than one. Another example of a tetragonally distorted pyrochlore with c/a less than one was found by C. R. Robbins of this laboratory, in a specimen of $2\text{Bi}_2\text{O}_3 \cdot \text{GeO}_2$ quenched from the liquid.

TABLE 1. X-Ray diffraction powder data for the compound $5\text{Bi}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$ ($\text{CuK}\alpha$ radiation)

d	I/I_0	hkl	d	I/I_0	hkl
19.54	1	-----	1.6393	20	622
6.99	9	-----	1.5943	11	226
5.91	1	-----	1.5551	7	444
3.800	4	202			
3.440	2	301	1.4918	2	604
			1.4731	1	406
3.214	3	113	1.3634	3	800
3.111	100	222	1.3117	1	008
3.013	4	-----	1.2800	2	822
2.786	3	-----			
2.728	37	400	1.2483	3	662
			1.2293	4	626
2.624	22	004	1.2206	4	840
2.372	5	204	1.2110	2	804
2.292	5	323	1.1819	2	408
1.9297	19	440			
1.8915	23	404	1.1072	2	844
			1.0844	1	448
1.8645	3	-----	1.0484	2	10, 2, 2
1.7098	3	-----			

3.3. Compound $\text{Bi}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5$

Although this composition has not been found in nature, the analogous composition $\text{Bi}_2\text{O}_3 \cdot \text{Ta}_2\text{O}_5$ has

been found and is called bismutotantalite. Both Dihlstrom [1] and Aurivillius [2] attempted to synthesize BiNbO_4 and BiTaO_4 but found that the synthetic compounds were different from the naturally occurring bismutotantalite, which is orthorhombic [12] and apparently isostructural with stibiotantalite (SbTaO_4) and antimony tetroxide (Sb_2O_4) [Dihlstrom, 1].

a. Low-Temperature Orthorhombic Modification

The low-temperature orthorhombic modification, was found in all solid-state preparations of the 1:1 composition heated below about 1,020 °C. However, once the high-temperature modification was formed the transformation could not be reversed by heating at lower temperatures. The X-ray diffraction powder pattern of the low-temperature modification is given in table 2, indexed on the basis of an orthorhombic unit cell with $a=4.980$ Å, $b=11.70$ Å, and $c=5.675$ Å.

TABLE 2. X-Ray diffraction powder data for the low temperature orthorhombic form of $\text{Bi}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5$ ($\text{CuK}\alpha$ radiation)

d	I/I_0	hkl	d	I/I_0	hkl
5.84	12	020	1.6969	3	152
4.576	8	110	1.6934	16	123
3.740	20	101	1.6879	9	232
3.564	15	111			
3.153	100	121	1.6439	3	310
			1.6337	4	251
3.071	8	130	1.6106	5	133
2.924	40	040	1.6080	7	062
2.838	26	002	1.5933	2	301
2.758	7	012			
2.700	3	131	1.5772	14	242
			1.5377	20	321
2.553	21	022	1.5278	3	330
2.490	22	200	1.5140	11	143
2.412	2	112	1.4942	2	213
2.305	20	141			
2.294	8	032	1.4635	6	080
			1.4621	4	252
2.292	10	220	1.4411	2	072
2.272	3	122	1.4228	3	312
2.238	6	211	1.4190	2	004
2.123	1	221			
2.085	3	132	1.4120	2	153
			1.4089	2	014
2.037	24	042	1.4063	2	233
1.9852	3	151	1.4003	2	341
1.9689	6	231	1.3799	8	024
1.9485	2	060			
1.8967	27	240	1.3636	3	104/181
			1.3564	1	114
1.8721	17	202	1.3547	2	350
1.8486	8	212	1.3513	5	262
1.8070	3	052	1.3479	3	271
1.7800	13	222			
1.7694	14	103	1.3333	2	034
			1.3126	4	163
1.7492	4	113	1.3011	4	082
1.7302	34	161			

b. High-Temperature Triclinic Modification

From about 1,020 °C to the melting point, about 1,245 °C, the stable modification of $\text{Bi}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5$ is the triclinic form reported by Aurivillius [2]. The X-ray diffraction powder pattern, listed in table 3, was indexed on the basis of a triclinic unit cell with $a=7.61$ Å, $b=5.53$ Å, $c=7.91$ Å, $\alpha=89.88^\circ$, $\beta=77.43^\circ$, $\gamma=87.15^\circ$ as compared with the rather inaccurate values calculated by Aurivillius [2] from Weissenburg photographs of $a=7.7$ Å, $b=5.5$ Å, $c=7.9$ Å, $\alpha=89^\circ$, $\beta=77^\circ$, $\gamma=87^\circ$.

TABLE 3. *X-ray diffraction power data for the high temperature triclinic form of $\text{Bi}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5$ ($\text{CuK}\alpha$ radiation)*

d	I/I_0	hkl^a	d	I/I_0	hkl^a
7.41	21	100	2.219	7	
6.09	2	101	2.177	4	
4.544	8	110			
4.324	3	110	2.166	6	
3.867	14	002	2.115	15	
			2.073	11	
3.779	4	102	2.048	4	
3.710	15	200	2.011	12	
3.666	2	201			
3.187	68	012	1.9803	23	
3.154	100	102/210	1.9348	15	
			1.9019	3	
3.149	97	012	1.8919	6	
3.102	24	112	1.8635	21	
3.025	44	202			
3.013	56	210	1.8567	15	
2.763	33	020	1.8363	6	
			1.8164	4	
2.706	3	112	1.7974	6	
2.690	7	212	1.7878	23	
2.620	8	212/103			
2.590	2	021	1.7775	5	
2.549	6	120/121	1.7666	6	
			1.7471	6	
2.474	8	300	1.7345	8	
2.428	25	202	1.7208	4	
2.370	4	203/113			
2.326	4	302	1.7160	5	
2.301	2		1.7074	7	
			1.6857	9	
2.274	4		1.6822	7	
2.255	4		1.6732	9	
2.246	5		1.6690	7	

^a Due to the complexity of the pattern only those hkl values have been given which can be assigned with reasonable certainty.

3.4. Compound $4\text{Bi}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$

This compound was found to be stable from about 1,070 °C to the incongruent melting point of 1,183 °C. The X-ray diffraction powder pattern, listed in table 4, can be indexed on the basis of a hexagonal unit cell with $a=6.447\text{ \AA}$, $c=19.778\text{ \AA}$. There is no indication on the powder pattern that the true symmetry might have $a=\sqrt{3}\cdot 6.447\text{ \AA}=11.166\text{ \AA}$.

A compound with a similar X-ray diffraction powder pattern $\text{Ba}(\text{Nb}_{.75}\text{Li}_{.25})\text{O}_3$ has $a=\sqrt{3}\cdot 5.797\text{ \AA}=10.040\text{ \AA}$, $c=19.072\text{ \AA}$; the increase in a is represented by only one small peak in the powder diffraction pattern. These X-ray diffraction powder patterns are similar to those of the hexagonal com-

TABLE 4. *X-ray diffraction power data for the compound $4\text{Bi}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$ ($\text{CuK}\alpha$ radiation)*

d	I/I_0	hkl	d	I/I_0	hkl
9.86	13	002	1.5703	18	1, 1, 11
4.946	4	004	1.5324	14	224
3.294	93	006	1.4931	9	225
3.179	83	111	1.4869	5	308
3.063	100	112	1.4133	2	0, 0, 14
2.895	10	113	1.4000	4	227
2.699	73	114	1.3554	3	3, 0, 10
2.499	28	115	1.3503	4	228
2.471	6	008	1.2496	5	2, 2, 11
2.308	4	116	1.2340	10	2, 1, 13
2.125	11	117	1.2203	5	1, 1, 15
1.9778	7	0, 0, 10	1.2162	5	411
1.9616	29	118	1.2096	4	412
1.8610	57	300	1.2003	3	2, 2, 11
1.8158	11	119	1.1833	5	414
1.6857	27	1, 1, 10	1.1646	4	415
1.6483	8	0, 0, 12	1.1539	3	1, 1, 16
1.6210	39	306	1.0749	2	330
1.6070	11	221	1.0376	3	4, 1, 10
1.5913	11	222	1.0215	2	336
			1.0088	4	4, 1, 11

pounds $5\text{BaO} \cdot 2\text{Nb}_2\text{O}_5$ [13], $5\text{BaO} \cdot 2\text{Ta}_2\text{O}_5$ [14], Hex-BaTiO_3 [15] and $\text{Rhomb PbO} \cdot \text{Nb}_2\text{O}_5$ [11]. It can be assumed that all of these compounds are structurally related, the major difference being in the stacking sequence of layers of the large cations plus O^{2-} ions.

3.5. Compounds $\text{Bi}_2\text{O}_3 \cdot 5\text{Nb}_2\text{O}_5$ and $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$

The compound $\text{Bi}_2\text{O}_3 \cdot 5\text{Nb}_2\text{O}_5$ was found to be stable from room temperature to a dissociation temperature of about 1,095 °C. The unindexed X-ray diffraction powder pattern of this compound is listed in table 5. The compound $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$ was found to be stable from about 1,002 °C to the incongruent melting point of 1,242 °C. The unindexed X-ray diffraction powder pattern of this compound is given in table 6. The X-ray patterns of these two compounds are very complex and obviously of low symmetry. From the general appearance of the two patterns it can be concluded that these two compounds are structurally related and probably also structurally related to pure Nb_2O_5 .

TABLE 5. *X-ray diffraction powder data for the compound $\text{Bi}_2\text{O}_3 \cdot 5\text{Nb}_2\text{O}_5$ ($\text{CuK}\alpha$ radiation)*

d	I/I_0	d	I/I_0	d	I/I_0
12.4	15	3.319	15	2.843	45
12.2	15	3.276	15	2.781	60
8.55	15	3.196	50	2.763	15
3.945	100	3.073	20	2.722	15
3.921	45	3.062	30	2.601	20
3.854	30	3.001	90	2.566	5
3.599	30	2.964	35	2.487	5
3.523	20	2.940	65	2.424	5
3.453	20	2.900	5	2.373	45
3.367	80	2.859	30		

TABLE 6. *X-ray diffraction powder data for the compound $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$ ($\text{CuK}\alpha$ radiation)*

d	I/I_0	d	I/I_0	d	I/I_0
7.49	5	3.206	40	2.736	10
6.15	5	3.129	25	2.596	40
5.92	10	3.089	20	2.592	35
3.929	100	3.032	40	2.439	5
3.673	25	3.000	60	2.402	10
3.619	15	2.964	15	2.386	10
3.455	30	2.930	40	2.352	10
3.442	35	2.854	10	2.294	5
3.310	10	2.788	30	2.275	10
3.274	20	2.773	55		

3.6. Nb_2O_5

The stability relations of the various reported polymorphs of Nb_2O_5 have been summarized by several workers [16, 17, 18, 19]. Bi_2O_3 , unlike PbO [11], has no catalytic action on the thermal stability of the various modifications of Nb_2O_5 . Since it has been concluded [11, 16, 19] that the high-temperature monoclinic form of Nb_2O_5 ($\text{H-Nb}_2\text{O}_5$) is the only stable form, no phase transformation temperature has been indicated. The X-ray powder pattern and unit cell dimensions of the stable form were previously reported [11].

4. Discussion of Phase Equilibria

The phase equilibrium diagram of the binary system $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ is shown in figure 1. The experimental data from which this diagram was constructed are given in table 7. The designation Per. in table 7 stands for the perovskite structure type and signifies that the material which crystallizes in this structure type must have been in the liquid state when quenched (see discussion of metastable compounds in section 5). The system contains one compound which melts congruently, $\text{Bi}_2\text{O}_3\cdot\text{Nb}_2\text{O}_5$; three compounds which melt incongruently, $5\text{Bi}_2\text{O}_3\cdot 3\text{Nb}_2\text{O}_5$, $4\text{Bi}_2\text{O}_3\cdot 9\text{Nb}_2\text{O}_5$, and $\text{Bi}_2\text{O}_3\cdot 6\text{Nb}_2\text{O}_5$; and one compound which dissociates before melting, $\text{Bi}_2\text{O}_3\cdot 5\text{Nb}_2\text{O}_5$. In addition $\text{Bi}_2\text{O}_3\cdot\text{Nb}_2\text{O}_5$ has two

polymorphs and $4\text{Bi}_2\text{O}_3\cdot 9\text{Nb}_2\text{O}_5$ and $\text{Bi}_2\text{O}_3\cdot 6\text{Nb}_2\text{O}_5$ both apparently have minimum temperatures of stability.

The high-temperature cubic polymorph of Bi_2O_3 is stabilized by the addition of Nb_2O_5 in solid solution. When specimens containing 1, 2, 3, and 4 mole percent Nb_2O_5 are quenched from the region between the monoclinic-cubic phase transformation and the solidus temperature the resultant material is tetragonal with the unit cell dimensions shown in table 8. However, high-temperature X-ray patterns show the compositions to be really cubic at these temperatures. The unit cell dimensions of the cubic and pseudocubic solid solutions from 5 mole percent Nb_2O_5 to 25 mole percent Nb_2O_5 are also given in table 8.

TABLE 7. Experimental data for compositions in the binary system $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$

Composition		Heat treatment				Results					
Bi ₂ O ₃	Nb ₂ O ₅	Calcine ^a		Quench ^b		Physical observation	X-ray diffraction analyses ^c				
		Temp	Time	Temp	Time						
<i>Mole %</i>	<i>Mole %</i>	<i>°C</i>	<i>hr</i>	<i>°C</i>	<i>hr</i>						
100	0			826	0.083	just begun to melt	Mon-Bi ₂ O ₃				
99	1	700	3	924	.083	melted	Do.				
				721	16.0	no melting	Mon-Bi ₂ O ₃				
				725	16.0	do	Tet-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃				
				773	2.0	do	Tet-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃ (tr)				
				827	0.083	just begun to melt	Tet-Bi ₂ O _{3ss}				
				833	.017	partially melted	Tet-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃				
				840	.017	considerably melted					
				850	.017	almost completely melted	Tet-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃				
				861	.017	completely melted (?)					
				880	.017	completely melted					
98	2	700	3	721	16.0	no melting	Mon-Bi ₂ O ₃				
				725	16.0	do	Tet-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃				
				773	2.0	do	Tet-Bi ₂ O _{3ss}				
				834	0.017	do	Do.				
				840	.017	just begun to melt	Do.				
				850	.017	partially melted					
				861	.067	do	Tet-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃				
				880	.017	almost completely melted					
				901	.017	completely melted					
				97	3	700	3	700	16.5	no melting	Mon-Bi ₂ O ₃ +b.c.c.-Bi ₂ O _{3ss}
712	17.0	do	Mon-Bi ₂ O ₃ +C-Bi ₂ O _{3ss}								
775	64.0	do	Tet-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃								
834	0.083	do	Tet-Bi ₂ O _{3ss}								
840	.017	do									
850	.017	just begun to melt									
861	.017	partially melted	Tet-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃ (tr)								
880	.017	do									
900	.017	completely melted (?)									
96	4	700	3					700	16.5	no melting	b.c.c. Bi ₂ O _{3ss} (<i>a</i> =10.263Å)+C-Bi ₂ O _{3ss} (tr)
				712	17.0	do	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃				
				775	64.0	do	Tet-Bi ₂ O _{3ss}				
				840	0.017	do	Do.				
				861	.033	partially melted					
				880	.017	do					
				899	.017	almost completely melted					
				920	.017	completely melted (?)					
				95 (19.1)	5	700	3	615/485	1/16	no melting	b.c.c. Bi ₂ O _{3ss} +C-Bi ₂ O _{3ss}
								500	2.0	do	Mon-Bi ₂ O ₃ +C-Bi ₂ O _{3ss} +b.c.c. Bi ₂ O _{3ss} (tr)
567	15.5	do	b.c.c. Bi ₂ O _{3ss} +C-Bi ₂ O _{3ss}								
596	0.5	do	Mon-Bi ₂ O ₃ +C-Bi ₂ O _{3ss} +b.c.c. Bi ₂ O _{3ss} (tr)								
632	1.0	do	Do.								
693	1.0	do	Mon-Bi ₂ O ₃ +C-Bi ₂ O _{3ss}								
700	3.0	do	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃								
782	16.0	do	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃ (tr)								
850	0.167	do	C-Bi ₂ O _{3ss} (poorly crystalline)								
860	.167	do	Do.								
869	.167	partially melted	Do.								
885	.017	considerably melted	C-Bi ₂ O _{3ss} +Tet-Bi ₂ O _{3ss} (tr)								
885	.167	tube leaked	C-Bi ₂ O _{3ss} +Tet-Bi ₂ O _{3ss}								
903	.033	considerably melted	(from outside of tube only) Tet-Bi ₂ O _{3ss}								
920	.033	do	C-Bi ₂ O _{3ss} +Tet-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃								
941	.067	completely melted									
1,008	.017	do	C-Bi ₂ O _{3ss} +Tet-Bi ₂ O _{3ss}								

See footnotes at end of table.

TABLE 7. Experimental data for compositions in the binary system $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ —Continued

Composition		Heat treatment				Results	
Bi_2O_3	Nb_2O_5	Calcine ^a		Quench ^b		Physical observation	X-ray diffraction analyses ^c
		Temp	Time	Temp	Time		
<i>Mole %</i> 92.31 (12:1)	<i>Mole %</i> 7.69	$^{\circ}\text{C}$ 700	<i>hr</i> 3	$^{\circ}\text{C}$	<i>hr</i>		
				603	65.0	no melting	C-Bi ₂ O _{3ss} +b.c.c. Bi ₂ O _{3ss}
				650	44.0	do	Mon-Bi ₂ O ₃ +C-Bi ₂ O _{3ss}
				681	17.0	do	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃
				783	1.0	do	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃ (tr)
				889	0.5	do	C-Bi ₂ O _{3ss}
				904	.25	just begun to melt	Do,
				912	.25	partially melted	C-Bi ₂ O _{3ss} +Tet-Bi ₂ O _{3ss} (tr)
				941	.167	do	C-Bi ₂ O _{3ss} +Tet-Bi ₂ O _{3ss}
				956	.083	do	C-Bi ₂ O _{3ss} +Tet-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃
				975	.017	completely melted (?)	
90.91 (10:1)	9.09	700	3				C-Bi ₂ O _{3ss} +b.c.c. Bi ₂ O _{3ss} +b.c.c./-Bi ₂ O _{3ss} (tr)
				603	65.0	no melting	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃ +b.c.c. Bi ₂ O _{3ss} (tr)+b.c.c./-Bi ₂ O _{3ss} (tr)
				650	44.0	do	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃ +b.c.c./-Bi ₂ O _{3ss} (tr)
				681	17.0	do	C-Bi ₂ O _{3ss} +b.c.c./-Bi ₂ O _{3ss} (tr)
				869	17.0	do	C-Bi ₂ O _{3ss}
				904	0.133	do	Do,
				937	.33	partially melted	C-Bi ₂ O _{3ss} +Tet-Bi ₂ O _{3ss}
				965	.017	do	Do,
				976	.033	do	
				996	.033	almost completely melted	
88	12	700	3	1,012	.033	completely melted	C-Bi ₂ O _{3ss} +b.c.c./-Bi ₂ O _{3ss} (tr)
				622	18	no melting	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃
				928	16	do	C-Bi ₂ O _{3ss}
				944	0.417	do	Do,
				960	.417	do	Do,
				988	.083	partially melted	C-Bi ₂ O _{3ss} +Tet-Bi ₂ O _{3ss}
				1,012	.067	do	
				1,041	.067	completely melted	
85	15	700	3				C-Bi ₂ O _{3ss}
				622	18	no melting	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃
				928	16	do	C-Bi ₂ O _{3ss}
				1,026	0.017	do	Do,
				1,033	.033	just begun to melt	C-Bi ₂ O _{3ss} +Tet-Bi ₂ O _{3ss} (tr)
				1,038	.033	partially melted	Do,
				1,054	.067	do	
				1,073	.067	completely melted	
84	16	700	6				C-Bi ₂ O _{3ss}
				600	16	no melting	C-Bi ₂ O _{3ss} +b.c.c. Bi ₂ O _{3ss}
				619	22	do	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃ (tr)
				1,004	1.0	do	C-Bi ₂ O _{3ss}
				1,050	0.083	partially melted	
				1,060	.083	do	
				1,069	.083	considerably melted	
				1,080	.083	completely melted	
83	17	700	6				C-Bi ₂ O _{3ss} +b.c.c. Bi ₂ O _{3ss}
				600	16	no melting	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃ (tr)
				619	22	do	C-Bi ₂ O _{3ss}
				1,004	1.0	do	
				1,050	0.083	do	
				1,060	.083	partially melted	
				1,070	.083	do	
				1,090	.083	completely melted	
82	18	700	6				C-Bi ₂ O _{3ss} +b.c.c./-Bi ₂ O _{3ss}
				599	16	no melting	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃ (tr)
				615	18	do	C-Bi ₂ O _{3ss}
				1,004	2	do	
				1,060	0.083	do	
				1,070	.083	partially melted	
				1,090	.083	almost completely melted	
81	19	700	6				C-Bi ₂ O _{3ss} +bcc Bi ₂ O _{3ss} (tr)
				599	16	no melting	C-Bi ₂ O _{3ss} +Mon-Bi ₂ O ₃ (tr)
				615	18	do	C-Bi ₂ O _{3ss}
				1,004	2	do	C'-Bi ₂ O _{3ss}
				1,070	0.083	do	C'-Bi ₂ O _{3ss}
				1,089	0.083	partially melted	
80	20	700	3				C'-Bi ₂ O _{3ss} +bcc Bi ₂ O _{3ss}
				503	70.5	no melting	Do,
				599	23	do	Do,
				869	17	do	C'-Bi ₂ O _{3ss}
				1,010	16	do	Do,
				1,056	0.5	do	Do,
				1,080	1.0	just begun to melt	
				1,101	0.167	completely melted	C'-Bi ₂ O _{3ss}
79	21	700	6				C'-Bi ₂ O _{3ss}
				1,050	2	no melting	
				1,080	0.083	do	
				1,090	.083	do	
				1,095	.083	just begun to melt	
				1,106	.083	almost completely melted	
				1,115	.083	completely melted	
78	22	700	6				C'-Bi ₂ O _{3ss}
				1,050	2	no melting	
				1,090	0.083	do	
				1,115	.083	almost completely melted	

See footnotes at end of table.

TABLE 7. *Experimental data for compositions in the binary system Bi₂O₃-Nb₂O₅—Continued*

Composition		Heat treatment				Results	
Bi ₂ O ₃	Nb ₂ O ₅	Calcine ^a		Quench ^b		Physical observation	X-ray diffraction analyses ^c
		Temp	Time	Temp	Time		
<i>Mole %</i> 77	<i>Mole %</i> 23	<i>° C</i> 700	<i>hr</i> 6	<i>° C</i>	<i>hr</i>		
				1,050	21.5	no melting	C'-Bi ₂ O _{3ss}
				1,115	0.083	almost completely melted	
				1,124	.083	completely melted(?)	
76	24	700	6	1,050	21.5	no melting	C'-Bi ₂ O _{3ss} +5Bi ₂ O ₃ ·3Nb ₂ O ₅ (tr)
				1,095	0.083	do	
				1,124	.083	considerably melted	
				1,135	.167	completely melted	
75	25	700	3	503	70.5	no melting	C'-Bi ₂ O _{3ss} +5Bi ₂ O ₃ ·3Nb ₂ O ₅
				1,080	0.5	do	Do.
				1,081	16.0	do	Do.
				1,090	0.5	do	Do.
				1,101	.5	partially melted	
				1,110	.75	considerably melted	
				1,135	.25	almost completely melted	
70	30	700	3	1,035	0.133	no melting	
				1,101	.083	just begun to melt	
				1,153	.083	partially melted	
				1,166	.083	considerably melted	
				1,174	.083	completely melted	
66.67 (2:1)	33.33	700	3	1,095	.083	no melting	C'-Bi ₂ O _{3ss} +5Bi ₂ O ₃ ·3Nb ₂ O ₅
				1,106	.083	partially melted	
				1,149	2.5	do	C'-Bi ₂ O _{3ss} +5Bi ₂ O ₃ ·3Nb ₂ O ₅
				1,160	0.33	do	Do.
				1,170	.167	considerably melted	
				1,180	.083	almost completely melted	
				1,191	.033	completely melted	
62.5 (5:3)	37.5	700	3	1,008	16.0	no melting	C'-Bi ₂ O _{3ss} +5Bi ₂ O ₃ ·3Nb ₂ O ₅ +L-Bi ₂ O ₃ ·Nb ₂ O ₅
				1,146	1.0	do	5Bi ₂ O ₃ ·3Nb ₂ O ₅
				1,150	64.0	do	5Bi ₂ O ₃ ·3Nb ₂ O ₅ +C'-Bi ₂ O _{3ss} (tr)+H-Bi ₂ O ₃ ·Nb ₂ O ₅ (tr)
				1,170	0.167	do	5Bi ₂ O ₃ ·3Nb ₂ O ₅
				1,180	.083	do	
				1,191	.033	do	
				1,196	.083	partially melted	5Bi ₂ O ₃ ·3Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ (tr)+C'-Bi ₂ O _{3ss} (tr)
				1,200	1.0	completely melted (?)	5Bi ₂ O ₃ ·3Nb ₂ O ₅ +C'-Bi ₂ O _{3ss} +H-Bi ₂ O ₃ ·Nb ₂ O ₅
60	40	700	3	945	16.0	no melting	5Bi ₂ O ₃ ·3Nb ₂ O ₅ +L-Bi ₂ O ₃ ·Nb ₂ O ₅
				1,057	0.667	do	Do.
				1,127	.5	do	5Bi ₂ O ₃ ·3Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅
				1,151	.5	do	Do.
				1,175	.333	do	Do.
				1,191	.033	do	Do.
				1,195	.5	partially melted	5Bi ₂ O ₃ ·3Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅
				1,200	.167	considerably melted	
				1,210	.083	almost completely melted	
				1,220	.167	completely melted	
55	45	700	3	1,189	0.083	no melting	
				1,195	.083	partially melted	
				1,230	.083	considerably melted	
				1,240	.083	completely melted	
50 (1:1)	50	700	3				L-Bi ₂ O ₃ ·Nb ₂ O ₅ +5Bi ₂ O ₃ ·3Nb ₂ O ₅ +L-Nb ₂ O ₅
				945	16.5	no melting	L-Bi ₂ O ₃ ·Nb ₂ O ₅
				1,001	16.0	do	Do.
				1,008	184.0	do	Do.
				1,024	2.833	do	Do.
				1,024	114.0	do	L-Bi ₂ O ₃ ·Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ (tr)
				1,036	15.5	do	H-Bi ₂ O ₃ ·Nb ₂ O ₅
				1,051	1.75	do	Do.
				1,156	20.0	do	Do.
				1,225	0.5	do	Do.
				1,241	.33	do	Do.
				1,252	.33	completely melted	Do.
		1,150	33				
				1,008	184.0	no melting	H-Bi ₂ O ₃ ·Nb ₂ O ₅
				1,240	0.167	do	
				1,246	.167	completely melted	
		1,200	3				
				1,001	16.0	no melting	H-Bi ₂ O ₃ ·Nb ₂ O ₅
				1,024	114.0	do	Do.
45	55	700	3				
				1,169	0.167	no melting	
				1,179	.167	do	
				1,182	.167	just begun to melt	
				1,230	.083	considerably melted	
				1,240	.083	almost completely melted	
				1,246	.167	completely melted	
40	60	700	3				
				1,145	17.0	no melting	H-Bi ₂ O ₃ ·Nb ₂ O ₅ +4Bi ₂ O ₃ ·9Nb ₂ O ₅
				1,169	0.167	do	Do.
				1,179	.167	do	

See footnotes at end of table.

TABLE 7. *Experimental data for compositions in the binary system Bi₂O₃-Nb₂O₅—Continued*

Composition		Heat treatment				Results	
Bi ₂ O ₃	Nb ₂ O ₅	Calcine ^a		Quench ^b		Physical observation	X-ray diffraction analyses ^c
		Temp	Time	Temp	Time		
<i>Mole %</i> 40	<i>Mole %</i> 60	<i>°C</i>	<i>hr</i>	<i>°C</i>	<i>hr</i>		
				1, 181 1, 194 1, 201 1, 212 1, 223	.083 .083 .167 .083 .083	partially melted considerably melted do. almost completely melted completely melted	H-Bi ₂ O ₃ ·Nb ₂ O ₅ +4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Per H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Per Do.
36	64	700	3	1, 173 1, 177 1, 179 1, 182 1, 185	.083 .083 .083 .167 .083	no melting do. do. partially melted completely melted	H-Bi ₂ O ₃ ·Nb ₂ O ₅ +4Bi ₂ O ₃ ·9Nb ₂ O ₅
33.33 (1:2)	66.67	700	3	1, 145 1, 180 1, 194	17.0 0.083 .083	no melting considerably melted completely melted	4Bi ₂ O ₃ ·9Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Per Per+H-Bi ₂ O ₃ ·Nb ₂ O ₅
32	68	700	3	1, 149 1, 149	2.0 17.0	no melting do.	4Bi ₂ O ₃ ·9Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ (tr) Do.
		1, 150	33	1, 170 1, 175 1, 181 1, 186	0.167 .167 .167 .083	no melting do. just begun to melt completely melted	
31.25 (5:11)	68.75	700	3	1, 149 1, 149	2.0 17.0	no melting do.	4Bi ₂ O ₃ ·9Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ (tr)
30.77 (4:9)	69.23	700	3	1, 001 1, 040 1, 061 1, 075 1, 149 1, 151 1, 151 1, 170 1, 180	23.0 1.0 40.0 64.0 2.0 16.0 70.0 0.167 .083	no melting do. do. do. do. do. do. do. partially melted (metastable melting of non-reacted components)	L-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ +4Bi ₂ O ₃ ·9Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ Do. 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Per
		1, 150	77	1, 001 1, 061 1, 075 1, 180 1, 185 1, 185 1, 190 1, 190 1, 194 1, 210	23 40 64 0.033 .033 1.0 0.083 1.0 0.167 do.	no melting do. do. do. partially melted considerably melted do. do. completely melted do.	4Bi ₂ O ₃ ·9Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ +Bi ₂ O ₃ ·Nb ₂ O ₅ (?) 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ (tr) 4Bi ₂ O ₃ ·9Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ +Per Per+4Bi ₂ O ₃ ·9Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ Per+H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ Do.
30	70	700	3	1, 149 1, 152	2.0 18.0	no melting do.	4Bi ₂ O ₃ ·9Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅
		1, 150	33	1, 180 1, 185 1, 200	0.167 .167 .25	no melting partially melted completely melted	
28.57 (2:5)	71.43	700	3	1, 083	16.0	no melting	H-Bi ₂ O ₃ ·Nb ₂ O ₅ +4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ +Bi ₂ O ₃ · 6Nb ₂ O ₅ (?) 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ Do. Do. Do.
		1, 142	16	1, 102 1, 149 1, 150 1, 150	1.0 17.0 2.0 18.0	do do do do	
				1, 180 1, 187 1, 200 1, 210	0.167 .167 .167 .167	no melting partially melted almost completely melted completely melted	Per+H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅
25 (1:3)	75	700	3	1, 085 1, 092	1.0 65.0	do do	L-Bi ₂ O ₃ ·Nb ₂ O ₅ +5Bi ₂ O ₃ ·3Nb ₂ O ₅ +L-Nb ₂ O ₅
				1, 001 1, 083	18.0 16.0	no melting do.	L-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ · 6Nb ₂ O ₅ (?) H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ +4Bi ₂ O ₃ ·9Nb ₂ O ₅ (tr) 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ · 6Nb ₂ O ₅ (?) 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ Bi ₂ O ₃ ·6Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ Per+Bi ₂ O ₃ ·6Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ Do.
		1, 150	33	1, 105 1, 173 1, 200 1, 219 1, 231 1, 388	1.0 0.33 .5 .667 .583 .167	no melting do. partially melted considerably melted almost completely melted completely melted	H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ +Bi ₂ O ₃ ·Nb ₂ O ₅ (tr) 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅
				1, 001 1, 092 1, 180 1, 185 1, 230 1, 240	18.0 65.0 0.167 .25 .167 .167	no melting do. do. partially melted almost completely melted completely melted	H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Unknown 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ +Bi ₂ O ₃ ·Nb ₂ O ₅ (tr) 4Bi ₂ O ₃ ·9Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅

See footnotes at end of table.

TABLE 7. *Experimental data for compositions in the binary system Bi₂O₃-Nb₂O₅—Continued*

Composition		Heat treatment				Results			
Bi ₂ O ₃	Nb ₂ O ₅	Calcine ^a		Quench ^b		Physical observation	X-ray diffraction analyses ^c		
		Temp	Time	Temp	Time				
<i>Mole %</i> 20	<i>Mole %</i> 80	<i>°C</i> 700 910	<i>hr</i> 3 9	<i>°C</i>	<i>hr</i>				
18.18 (1:4)	81.82	700 910	3 9	999	19.0	no melting			
				1,050	4.0	do			
				1,060	18				
				1,150	24	1,075	88.5	no melting	
				1,246	0.167	partially melted	H-Nb ₂ O ₅ +Per+H-Bi ₂ O ₃ ·Nb ₂ O ₅		
				1,299	0.167	considerably melted			
				1,310	.167	do			
				1,319	.083	do			
				1,325	.167	almost completely melted			
				1,334	.167	completely melted(?)	Per+H-Bi ₂ O ₃ ·Nb ₂ O ₅ +H-Nb ₂ O ₅ +unknown Do.		
1,359	.167	completely melted							
18.18 (2:9)	81.82	700 910	3 9	999	19.0	no melting	L-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ +H-Nb ₂ O ₅		
				1,050	4.0	do	Bi ₂ O ₃ ·5Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ Do.		
				1,060	18				
				1,150	24	1,075	88.5	no melting	
				1,319	0.167	partially melted			
				1,334	.25	do	H-Nb ₂ O ₅ +Per+H-Bi ₂ O ₃ ·Nb ₂ O ₅		
				1,339	.083	considerably melted			
				1,350	.167	almost completely melted	Per+H-Bi ₂ O ₃ ·Nb ₂ O ₅ +H-Nb ₂ O ₅		
				1,359	.25	completely melted(?)	Per+H-Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +unknown Do.		
				1,378	.083	completely melted			
16.67 (1:5)	83.33	700 910	3 9	1,088	21.0	no melting	Bi ₂ O ₃ ·5Nb ₂ O ₅ +H-Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅		
				1,096	16.0	do	Bi ₂ O ₃ ·6Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ +4Bi ₂ O ₃ ·9Nb ₂ O ₅		
				1,105	16.0	do	Bi ₂ O ₃ ·6Nb ₂ O ₅ +4Bi ₂ O ₃ ·9Nb ₂ O ₅ Do.		
				1,153	90.0	do			
				999	19.0	no melting	Bi ₂ O ₃ ·5Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ (tr)+H-Nb ₂ O ₅ (tr)		
				1,050	4.0	do	Bi ₂ O ₃ ·5Nb ₂ O ₅ Do.		
				1,060	18				
				1,075	88.5	no melting	Bi ₂ O ₃ ·5Nb ₂ O ₅ Do.		
				1,088	21.0	do	Bi ₂ O ₃ ·5Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅ (tr)		
				1,096	16.0	do	Do.		
1,105	16.0	do							
1,153	90.0	do	Bi ₂ O ₃ ·6Nb ₂ O ₅ +4Bi ₂ O ₃ ·9Nb ₂ O ₅						
15.39 (2:11)	84.61	700 1060 1150	6 23 24	1,180	0.167	no melting			
				1,185	.167	just begun to melt	Bi ₂ O ₃ ·6Nb ₂ O ₅ +Per		
				1,230	.167	partially melted			
				1,240	.083	partially melted	Bi ₂ O ₃ ·6Nb ₂ O ₅ +Per		
				1,245	.167	do	Per+H-Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O		
				1,339	.167	considerably melted			
				1,351	.083	do			
				1,378	.05	almost completely melted			
				1,401	.167	completely melted	Per+H-Nb ₂ O ₅ +H-Bi ₂ O ₃ ·Nb ₂ O ₅ +unknown		
							Bi ₂ O ₃ ·5Nb ₂ O ₅ +Bi ₂ O ₃ ·6Nb ₂ O ₅		
14.29 (1:6)	85.71	700	3	1,339	0.167	partially melted			
				1,351	.033	considerably melted			
				1,400	.167	completely melted	L-Nb ₂ O ₅ +L-Bi ₂ O ₃ ·Nb ₂ O ₅ +5Bi ₂ O ₃ ·3Nb ₂ O ₅ (tr)		
				1,000	21.0	no melting	Bi ₂ O ₃ ·5Nb ₂ O ₅ +H-Nb ₂ O ₅		
				1,005	1.0	do	Bi ₂ O ₃ ·6Nb ₂ O ₅ +H-Nb ₂ O ₅ (tr)+Bi ₂ O ₃ ·5Nb ₂ O ₅ (tr)		
				1,014	1.5	do	Do.		
				1,019	1.0	do	Do.		
				1,040	1.0	do	Do.		
				1,075	16.0	do	Bi ₂ O ₃ ·6Nb ₂ O ₅		
				1,174	16.5	do	Do.		
1,201	1.0	do	Bi ₂ O ₃ ·6Nb ₂ O ₅						
1,220	1.0	do	Do.						
1,248	1.0	partially melted	H-Nb ₂ O ₅ +Per+H-Bi ₂ O ₃ ·Nb ₂ O ₅						
1,277	1.0	do	Do.						
1,282	68.0	do	Do.						
1,305	0.33	do	Do.						
1,311	.33	partially melted							
1,322	.5	do							
1,351	1.0	considerably melted	H-Nb ₂ O ₅ +Per+H-Bi ₂ O ₃ ·Nb ₂ O ₅						
1150	33	700	3	1,000	21	no melting	Bi ₂ O ₃ ·6Nb ₂ O ₅ +Bi ₂ O ₃ ·5Nb ₂ O ₅ +H-Nb ₂ O ₅ (tr)		
				1,075	16.0	do	Bi ₂ O ₃ ·6Nb ₂ O ₅ Do.		
				1,240	2.0	do			
				1,244	0.167	partially melted			
				1,350	.167	considerably melted			
				1,359	.167	do			
				1,378	.05	do			
				1,400	.167	almost completely melted			
				1,425	.083	completely melted			

TABLE 7. Experimental data for compositions in the binary system $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ —Continued

Composition		Heat treatment				Results	
Bi_2O_3	Nb_2O_5	Calcine ^a		Quench ^b		Physical observation	X-ray diffraction analyses ^c
		Temp	Time	Temp	Time		
<i>Mole %</i> 9.09 (1:10)	<i>Mole %</i> 90.91	$^{\circ}\text{C}$ 700	<i>hr</i> 3	$^{\circ}\text{C}$	<i>hr</i>		$\text{L-Nb}_2\text{O}_5 + \text{L-Bi}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5 + 5\text{Bi}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5 (\text{tr})$
				898	16.0	no melting	$\text{Bi}_2\text{O}_3 \cdot 5\text{Nb}_2\text{O}_5 + \text{H-Nb}_2\text{O}_5$
				1,005	1.0	do	$\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5 + \text{H-Nb}_2\text{O}_5$
				1,014	1.5	do	Do,
				1,019	1.0	do	Do,
				1,284	0.5	partially melted	
				1,295	.5	do	
				1,301	.33	do	
				1,310	.33	do	
		1,150	24	1,240	0.167	no melting	$\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5 + \text{H-Nb}_2\text{O}_5$
				1,245	.167	partially melted	
				1,401	.083	considerably melted	
				1,426	.083	do	
				1,451	.083	completely melted	
5	95	700	3				
		1,150	24	1,240	0.167	no melting	$\text{H-Nb}_2\text{O}_5 + \text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$
				1,245	.167	just begun to melt	
				1,425	.083	partially melted	
				1,451	.083	considerably melted	
				1,480	.083	completely melted	
0	100			1,480	.083	no melting	
				1,484	.083	do	
				1,486	.083	completely melted	
				1,489	.083	do	
				1,491	.083	do	

^a All calcined specimens were heated and cooled at the rate of approximately $4^{\circ}\text{C}/\text{min}$. All specimens were first calcined at 700°C and then small portions of this calcine were recalcined at one or more desired higher temperatures.

^b All specimens were quenched in sealed Pt tubes.

^c The phases identified are given in the order of the amount present at room temperature. The phases are not necessarily those present at the temperature to which the specimen was heated. C—cubic, C'—pseudocubic, b.c.c.—body-

centered cubic ($a=10.263 \text{ \AA}$), b.c.c.—body-centered cubic ($a=10.15\text{--}10.19 \text{ \AA}$), Tet—tetragonal, Mon—monoclinic, L—low-temperature polymorph, H—high-temperature polymorph, Per—perovskite ($a=3.94 \text{ \AA}$), a composition of approximately $\text{Bi}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$ always metastable in this system and occurs only upon quenching the liquid, ss—solid solution, tr—trace, just barely discernable in X-ray pattern.

TABLE 8. Unit cell dimensions of tetragonal and cubic Bi_2O_3 solid solutions

Composition		Heat treatment, quench		Unit cell dimensions	
Bi_2O_3	Nb_2O_5	Temp	Time	<i>a</i>	<i>c</i>
<i>Mole %</i>	<i>Mole %</i>	$^{\circ}\text{C}$	<i>hr</i>	\AA	\AA
99	1	773	2	10.938	5.632
98	2	773	2	10.921	5.638
97	3	775	64	5.461	5.646
96	4	775	64	5.464	5.647
95	5	782	16	^a 5.525	-----
92.31	7.69	783	1	5.540	-----
90.91	9.09	869	17	5.533	-----
88	12	928	16	5.521	-----
85	15	928	16	5.510	-----
84	16	1,004	1	5.504	-----
83	17	1,004	1	5.499	-----
82	18	1,004	2	5.494	-----
81	19	1,004	2	5.490	-----
80	20	1,010	16	^b 5.483	-----
79	21	1,050	2	5.480	-----
78	22	1,050	2	5.477	-----
77	23	1,050	21.5	5.471	-----
76	24	1,050	21.5	5.469	-----
75	25	1,081	16	5.469	-----

^a This material was poorly crystalline and the value given is an average-value for the cubic and tetragonal phases.

^b From 20 to 25 mole percent Nb_2O_5 the parameters represent the values measured for the pseudocubic cell.

The melting points of the solid solutions increase from the melting point of pure Bi_2O_3 , 825°C [20], to about $1,055^{\circ}\text{C}$ at 17 mole percent Nb_2O_5 . A morphotropic transformation occurs in the solid

solution at this point curving to a eutectoid at about 610°C and 19.5 mole percent Nb_2O_5 . The cubic-monoclinic transformation temperature is lowered from about 730°C to the above-mentioned eutectoid although there is very little solid solution in the monoclinic phase.

The solid solution higher in Nb_2O_5 content is designated C'ss in table 7. It is apparently only pseudocubic with several very small superstructure peaks in the X-ray diffraction pattern corresponding to *d* spacings of about 8.4 \AA , 2.69 \AA , and 2.35 \AA . The two phase region between the two solid solution fields is too narrow to be found by experimentation and is shown as dashed lines in figure 1. The C'ss is apparently stable from room temperature to the solidus which extends to about $1,096^{\circ}\text{C}$ at 23 mole percent Nb_2O_5 . The peritectic for this solidus occurs at about 20 mole percent Nb_2O_5 .

The liquidus rises smoothly from the $1,096^{\circ}\text{C}$ peritectic to another peritectic at 36.5 mole percent Nb_2O_5 and $1,193^{\circ}\text{C}$ corresponding to the incongruent melting temperature of the compound $5\text{Bi}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$. There is little or no solid solution on either side of this compound, or any other of the compounds in the binary system, as shown by the similarity of the unit cell dimensions of the pure compound to those of the same compound in a two phase region.

The liquidus again rises smoothly from the $1,193^{\circ}\text{C}$ peritectic to the congruent melting point of $\text{Bi}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5$ at $1,245^{\circ}\text{C}$. This compound was observed to crystallize in two polymorphic forms.

The low-temperature orthorhombic form was found to transform to the triclinic form at about 1,020 °C. However this phase transformation could not be reversed. Neither polymorph appeared changed after 184 hr at 1,008 °C, but a small amount of the high-temperature form was present in the original low form after 114 hr at 1,024 °C (see table 7). Because of the inability to reverse the phase transformation the polymorphic change is shown as a dashed line in figure 1.

The liquidus curve falls smoothly from 1,245 °C to a eutectic at 1,180 °C and about 64 mole percent Nb_2O_5 . The liquidus then rises very shallowly to a peritectic point at about 68 mole percent Nb_2O_5 and 1,183 °C, the incongruent melting temperature of the $4\text{Bi}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$ compound. This compound needs a long period of heating time at relatively high temperatures in order to form a single phase. It also takes a relatively long time to be completely transformed to liquid plus the $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$ com-

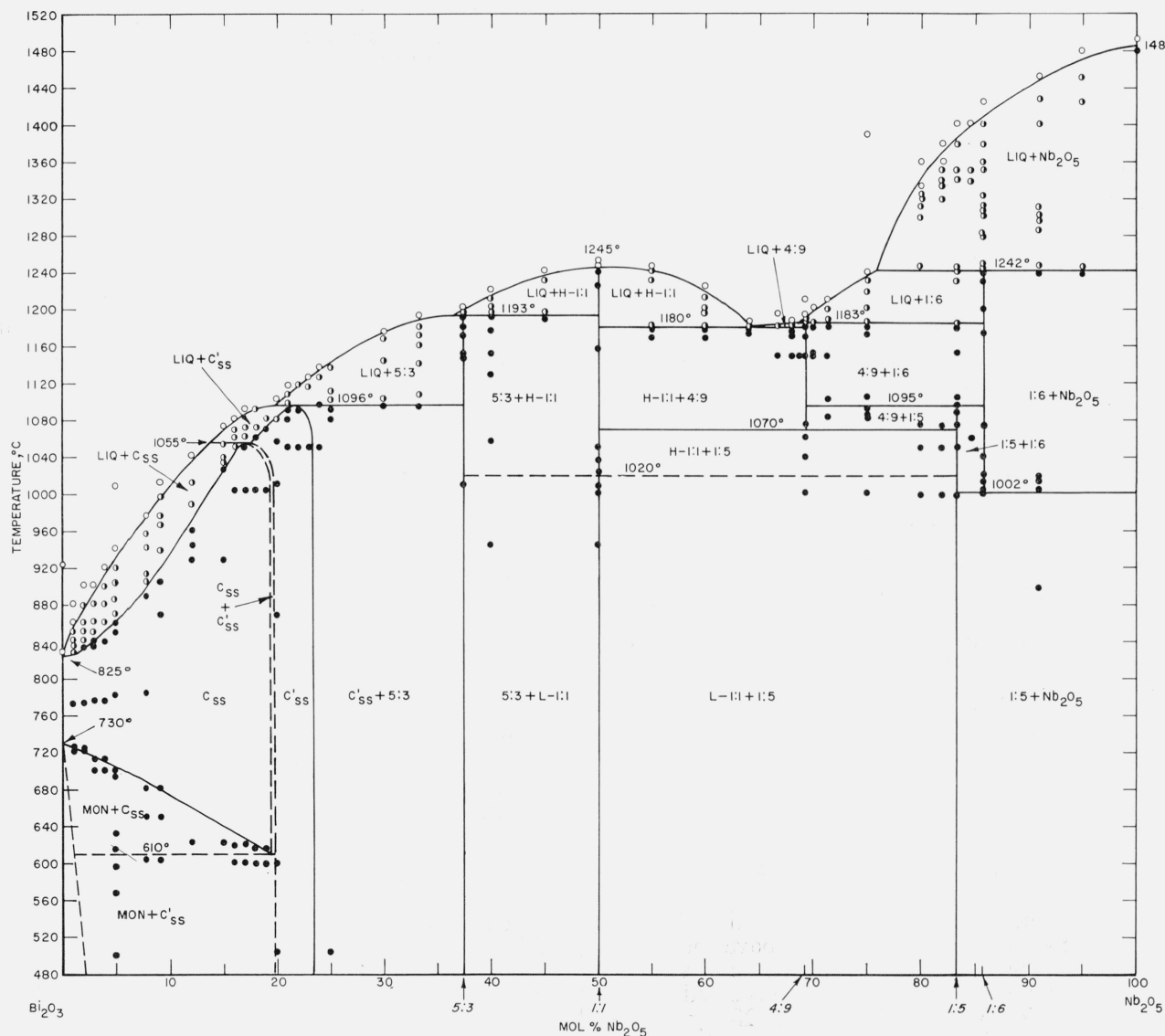


FIGURE 1. Phase equilibrium diagram for the system $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5$

- no melting
- ◐—partially melted
- completely melted
- L—low temperature modification
- H—high temperature modification
- C—cubic
- C'—pseudocubic
- Mon—monoclinic
- LIQ—liquid

pound (see table 7). The hexagonal $4\text{Bi}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$ compound is not formed at all below about $1,070^\circ\text{C}$. Specimens preheated to form a single phase are slowly decomposed to triclinic $\text{Bi}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5$ and the $\text{Bi}_2\text{O}_5 \cdot 5\text{Nb}_2\text{O}_5$ compound, when heated below about $1,070^\circ\text{C}$. The $4\text{Bi}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$ compound can therefore be concluded to have a minimum temperature of stability at about $1,070^\circ\text{C}$.

The compound $\text{Bi}_2\text{O}_3 \cdot 5\text{Nb}_2\text{O}_5$ was found to have a maximum temperature of stability of about $1,095^\circ\text{C}$. The preformed compound slowly decomposed to $4\text{Bi}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$ and $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$ above this temperature, while the original 700° calcined material showed no $\text{Bi}_2\text{O}_3 \cdot 5\text{Nb}_2\text{O}_5$ at all when heated much above $1,095^\circ\text{C}$. The compound $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$ was found to have a minimum temperature of stability at about $1,002^\circ\text{C}$. A specimen heated for 21 hr at $1,000^\circ\text{C}$ contained only $\text{Bi}_2\text{O}_3 \cdot 5\text{Nb}_2\text{O}_5$ and $\text{H-Nb}_2\text{O}_5$, while heating for 1 hr at $1,005^\circ\text{C}$ was enough to form the $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$ phase with only traces of the other two. The preformed $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$ compound showed definite traces of $\text{Bi}_2\text{O}_3 \cdot 5\text{Nb}_2\text{O}_5$ and $\text{H-Nb}_2\text{O}_5$ after reheating for 21 hr at $1,000^\circ\text{C}$.

$\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$ was found to melt incongruently at $1,242^\circ\text{C}$ to a liquid containing approximately 76 mole percent Nb_2O_5 plus crystalline Nb_2O_5 with little or no Bi_2O_3 in solid solution. The liquidus between the $1,183^\circ\text{C}$ peritectic and the $1,242^\circ\text{C}$ peritectic is essentially a straight line. The liquidus rises smoothly from the last peritectic to the melting point of Nb_2O_5 , found to be $1,485^\circ\text{C}$ for the batch of Nb_2O_5 used for this study. As this Nb_2O_5 is essentially Ta free it is not surprising that this melting point is several degrees lower than that previously reported [11, 13, 16, 19].

It is interesting to note that although both BaO and PbO enter into solid solution in Nb_2O_5 [11, 13] the Bi_2O_3 does not. Considering that the radius and polarizability of Pb^{+2} and Bi^{+3} are very similar [20] this fact must be dependent on the difference in valence. It should also be noted that unlike PbO [11] Bi_2O_3 has no catalytic effect upon the temperature of the metastable phase transformations in Nb_2O_5 .

5. Metastable Phases

5.1. The Perovskite Phase

When compositions containing more than 50 mole percent Nb_2O_5 were quenched from above the solidus a metastable phase always formed from the liquid. The maximum amount of this phase occurred around the composition $\text{Bi}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$. The X-ray diffraction pattern of this phase could be interpreted as that of a poorly crystalline cubic perovskite with $a \approx 3.94\text{\AA}$. Specimens quenched from above about $1,380^\circ\text{C}$ (well above the liquidus) contained another metastable phase which had an X-ray diffraction pattern similar to the cubic perovskite, but with extra lines. The metastable perovskite in this system can be compared with the distorted perovskite compound $\text{La}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$, previously reported [21].

5.2. The System $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5\text{--Alcohol}$

A large number of metastable phases were found to occur in the $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ system if either methyl or ethyl alcohol was used for wet mixing of the end members, and the resultant material was pressed into a pellet and fired without first thoroughly drying the mixture. Two separate body centered cubic phases were observed in mixtures containing 3 to 25 mole percent Nb_2O_5 which had been wet mixed with methyl alcohol. The first phase, labeled b.c.c. in table 7, had a unit cell dimension of $a = 10.263\text{\AA}$. This phase decomposed quickly in quench runs above 750°C and did not affect the melting point measurements. However specimens containing 16 to 24 mole percent Nb_2O_5 originally mixed with methyl alcohol contained large amounts of a second body centered cubic phase (labeled b.c.c.' in table 7) with a about 10.15 to 10.19 \AA . These specimens were found to dissociate to unknown phases which had metastable melting points several hundred degrees below the melting values of specimens prepared without alcohol, and had to be discarded. For these latter compositions only the dry-mixed specimens are reported in table 7. Other unknown phases were found in mixtures containing 1 to 4 mole percent Nb_2O_5 which had been wet-mixed in ethyl alcohol and were also discarded for table 7.

It seems likely that Bi_2O_3 forms a series of complex compounds with methyl and ethyl alcohol and can incorporate Nb_2O_5 into these compounds. The first b.c.c. phase ($a = 10.263\text{\AA}$) seems to contain little or no Nb_2O_5 and probably contains only Bi_2O_3 and alcohol or carbon. The second (b.c.c.') phase apparently contained about 12 to 15 mole percent Nb_2O_5 (plus alcohol or carbon). The body-centered cubic phase appears to be built up by spheres of Bi^{+3} and O^{2-} ions with a large tetrahedrally coordinated hole in the center [6, 8]. This host lattice, by itself apparently thermodynamically unstable, is stabilized in some cases by the addition of a second component in the central hole. It is possible that this phase may therefore be a clathrate type compound. A more complete study by high-temperature X-ray diffraction, of the body-centered cubic phase with a large number of other oxides will be discussed in a future publication.

6. Summary

The system $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ was studied by means of solid state reactions, fusion characteristics, and X-ray diffraction data. The existence of five compounds in this system was shown. They are: $5\text{Bi}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$, which melts incongruently at $1,193^\circ\text{C}$ to $\text{Bi}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5$ and liquid containing about 36.5 mole percent Nb_2O_5 ; $\text{Bi}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5$ which melts congruently at $1,245^\circ\text{C}$, and has a phase transition (irreversible in laboratory time) at about $1,020^\circ\text{C}$ from a low-temperature orthorhombic structure to a high temperature triclinic form; $4\text{Bi}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$ which has a minimum temperature of stability at $1,070^\circ\text{C}$ and melts incongruently to $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$ and liquid containing about 68 mole percent Nb_2O_5 ; $\text{Bi}_2\text{O}_3 \cdot 5\text{Nb}_2\text{O}_5$ which

has a maximum temperature of stability, decomposing at 1095 °C to $4\text{Bi}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$ plus $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$; and $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$ which has a minimum temperature of stability at 1,002 °C and melts incongruently at 1,242 °C to Nb_2O_5 and a liquid containing about 76 mole percent Nb_2O_5 . The only eutectic in the system occurs at 1,180 °C and about 64 mole percent Nb_2O_5 .

Nb_2O_5 enters into solid solution in the high-temperature cubic form of Bi_2O_3 , raising the melting point to about 1,055 °C and lowering the monoclinic to cubic phase transition from about 730 °C to about 610 °C. A morphotropic transition occurs in the solid solution at about 19.5 mole percent to a pseudocubic form, and further solid solution occurs from 19.5 mole percent to about 23.5 mole percent Nb_2O_5 . The pseudocubic form of Bi_2O_3 solid solution is stable from room temperature to a maximum solidus temperature of 1,096 °C. No solid solution was observed in Nb_2O_5 or in any of the five binary compounds in the system.

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7. References

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